Synthesis and photoluminescence properties of novel far-red-emitting BaLaMgNbO$_6$:Mn$^{4+}$ phosphors for plant growth LEDs

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A series of far-red-emitting BaLaMgNbO$_6$:Mn$^{4+}$ (BLMN:Mn$^{4+}$) phosphors were successfully synthesized by a high-temperature solid-state reaction method. Crystal structure and luminescence properties of the obtained samples were systematically investigated. The emission spectra exhibited a strong narrow far-red emission band peaking at 700 nm with a full width at half-maximum (FWHM) of ~36 nm under 360 nm excitation. The optimal Mn$^{4+}$ concentration was about 0.4 mol%. The internal quantum efficiency and CIE chromaticity coordinates of the BLMN:0.4% Mn$^{4+}$ phosphor were 52% and (0.7222, 0.2777), respectively. In addition, the luminescence mechanism has been analyzed using a Tanabe–Sugano energy level diagram. Finally, by using a 365 nm near-ultraviolet InGaN chip combined with BLMN:0.4% Mn$^{4+}$ phosphors, a far-red LED device was fabricated.
concentration of Mn$^{4+}$ was about 0.4 mol%. The CIE chroma-
ticity coordinates and internal quantum efficiency (IQE) of
BLMN:0.4% Mn$^{4+}$ sample were (0.7222, 0.2777) and 52%,
respectively. Moreover, the concentration quenching mecha-
nism was discussed. In addition, the luminescence mechanism
was explained by the Tanabe–Sugano energy level diagram.
Thermal quenching characteristics were also analyzed. All these
investigations demonstrated that BLMN:Mn$^{4+}$ phosphors are
promising far-red-emitting materials for far-red LEDs for plant
growth.

Experimental
A series of BaLaMgNb$_1-x_0_6_x$Mn$^{4+}$ (BLMN:xMn$^{4+}$; x = 0.05%,
0.1%, 0.2%, 0.4%, 0.8%, and 1.0%) phosphors were successfully
synthesized through a high-temperature solid-state reaction
method. BaCO$_3$ (analytical reagent, AR), La$_2$O$_3$ (99.99%), MgO
(AR), Nb$_2$O$_5$ (AR), and MnCO$_3$ (AR) were used as the raw ma-
terials. According to the stoichiometric ratio, these raw materials
were weighted and ground in an agate mortar to achieve
uniformity. The obtained mixtures were transferred to the
alumina crucibles and pre-calcined at 500 °C for 3 h, then sin-
tered at 1500 °C for 6 h in air. Finally, the samples were cooled
to room temperature naturally in the furnace, and they were
reground again to obtained final samples for further characteriza-
tions.

The X-ray diffraction (XRD) patterns of the samples were
recorded on a Bruker D8 X-ray diffractometer using Cu Kz
radiation. The morphological properties of the samples were
analyzed by using a field-emission scanning electron micro-
scope (FE-SEM; TESCAN MAIA3). The photoluminescence (PL)
and PL excitation (PLE) spectra and decay lifetimes were
measured by an Edinburgh FS5 spectrometer equipped with
a 150 W continued-wavelength xenon lamp and a pulsed xenon
lamp, respectively. The IQE was measured by an Edinburgh FS5 spectrometer equipped with an integrating sphere coated with BaSO$_4$.

Results and discussion
Fig. 1 shows the XRD patterns of the as-prepared BLMN:xMn$^{4+}$
(x = 0.05%, 0.1%, 0.2%, 0.4%, 0.8%, and 1.0%) samples. It can be
seen that all the samples exhibited similar diffraction patterns,
indicating that increasing Mn$^{4+}$ ions concentration does not significantly influence the crystal structure.

To further analyze the crystal structure details of the as-
prepared samples, Rietveld refinement of BLMN:0.4% Mn$^{4+}$
was carried out. The refined results for the XRD profile of
BLMN:0.4% Mn$^{4+}$ are shown in Fig. 2, including the observed
data (dot), calculated patterns (black line), the difference between
the experimental and calculated data (blue line), and the posi-
tions of Bragg reflection (short vertical green line). The final
refinement data $R_{wp}$ and $R_p$ were determined to be 10.84% and
8.93%, respectively, indicating the refined results were reliable.

The final refined crystallographic data were listed in Table 1.

Fig. 3 presents the crystal structure of BLMN:0.4% Mn$^{4+}$. The
BLMN:0.4% Mn$^{4+}$ belongs to double-perovskite oxide and has
a cubic system with space group $Fm\bar{3}m$. The lattice parameters
are $a = b = c = 8.0620$ Å, $V = 523.99$ Å$^3$, $N = 4$ and $\alpha = \beta = \gamma = 90^\circ$. It can be found that Nb$^{5+}$ and Mg$^{2+}$ ions occupy octahedral sites with six oxygen atoms surrounded. BLMN has many [NbO$_6$] octahedral sites, which are suitable for Mn$^{4+}$ ions doping. Mn$^{4+}$ ions prefer to substitute for the Nb$^{5+}$ ions over
Mg$^{2+}$, Ba$^{2+}$ and La$^{3+}$ ions owing to the similar ionic radii (0.53 Å
for Mn$^{4+}$, 0.64 Å for Nb$^{5+}$, 0.72 Å for Mg$^{2+}$, 1.35 Å for Ba$^{2+}$
and 1.32 Å for La$^{3+}$). As well-known, the radius percentage

Table 1. Refined structural data of BLMN:0.4% Mn$^{4+}$ sample

| Formula | BLMN:0.4% Mn$^{4+}$ |
|---------|-------------------|
| Crystal system | Cubic |
| Space group | $Fm\bar{3}m$ |
| $a = b = c$ | 8.0620 Å |
| $\alpha = \beta = \gamma$ | 90° |
| $V$ | 523.99 Å$^3$ |
| $N$ | 4 |
| $R_{wp}$ | 10.84% |
| $R_p$ | 8.93% |
Mg, Nb, O, Mn elements were uniformly distributed on the surface of particles. The results further proved that the Mn⁴⁺ ions were well-doped in the BLMN host.

The crystal structure of BLMN:0.4% Mn⁴⁺.

The difference between the doped ions and the substituted ions should be less than 30%. The radius percentage difference between Mn⁴⁺ ions and Nb⁵⁺ ions can be estimated using the following equation:  

\[ D_t = \frac{R_e (\text{CN}) - R_d (\text{CN})}{R_e (\text{CN})} \times 100\% \]  

(1)

where \( D_t \) is the difference in radius percentage, \( R_e (\text{CN}) \) and \( R_d (\text{CN}) \) are the radius of the host ions and doped ions with different coordination number CN, respectively. The calculated \( D_t \) was determined to be around 17%, which was much smaller than 30%. Therefore, the Mn⁴⁺ ions were substitute for Nb⁵⁺ ions in the BLMN host lattice.

Fig. 4(a and b) shows the SEM images of the as-prepared BLMN:0.4% Mn⁴⁺ sample. It can be clearly seen that the obtained sample was agglomerated and the particle size ranged within 1–4 μm. Moreover, the corresponding element mapping results were shown in Fig. 4(c–h). The components of Ba, La, Mg, Nb, O, Mn elements were uniformly distributed on the surface of particles. The results further proved that the Mn⁴⁺ ions were well-doped in the BLMN host.

Fig. 5(a) shows the typical PLE and PL spectra of BLMN:0.4% Mn⁴⁺ sample. When monitored at 700 nm, the PLE spectrum exhibited two broad excitation bands in the region of 250 to 600 nm, which could be fitted by four Gaussian curves. The four deconvoluted Gaussian peaks centered at 327, 375, 472, and 520 nm could be ascribed to Mn–O charge transfer band (CTB), and the Mn⁴⁺ spin-allowed transitions of \( ^4A_2g \rightarrow ^4T_{1g} \), \( ^4A_2g \rightarrow ^2T_{2g} \), and \( ^4A_2g \rightarrow ^4T_{2g} \), respectively.⁴⁶ The PLE spectrum indicated that the BLMN:Mn⁴⁺ phosphors can be efficiently excited by near-UV or blue LED chips. When excited at 360 nm and 469 nm, the BLMN:Mn⁴⁺ phosphors showed an intense far-red emission peaking at 700 nm in the wavelength range of 650–800 nm, which was attributed to \( ^2E_g \rightarrow ^2A_{2g} \) transition of Mn⁴⁺ ions in the [MnO₆]⁸⁻ octahedral environment.⁴⁷–⁵⁰ Moreover, the full-width at half maximum (FWHM) was as narrow as ∼36 nm.

Fig. 5(b) shows PL spectrum of BLMN:0.4% Mn⁴⁺ phosphors and the absorption spectrum of phytochrome PFR. An obvious overlap between the absorption spectrum of phytochrome PFR and the emissions spectrum of BLMN:0.4% Mn⁴⁺ phosphors was observed, which suggested the BLMN:Mn⁴⁺ phosphors could be used as far-red emitting materials for plant growth LEDs. Fig. 5(c) shows the PL spectra of BLMN:Mn⁴⁺ phosphors with different Mn⁴⁺ doping concentrations under 360 nm excitation. There was no change in peak shape and position with increasing Mn⁴⁺ concentration except for the emission intensity. It can be clearly seen that the PL emission intensity increased gradually with increasing the doping concentration until it reached a maximum at \( x = 0.4% \), then began to decrease with further increasing Mn⁴⁺ content owing to the concentration quenching effect.⁵¹–⁵⁵ With increasing the doping concentration, the distance between Mn⁴⁺–Mn⁴⁺ ions decreased, the possibility of energy transfer between the nearest Mn⁴⁺ ions increased, leading to lower the luminescence efficiency. In the BLMN:Mn⁴⁺ phosphors the energy transfer mechanism can not be the radiation reabsorption, because there is no overlap between PLE and PL spectra of Mn⁴⁺ ions.⁵⁶ It might be related to exchange interaction or electric multipolar interaction. The critical distance (\( R_c \)) was roughly estimated by the following formula:⁵⁴

\[ R_c = 2 \left[ \frac{3V}{4\pi CN} \right]^{1/3} \]  

(2)

where \( V \) is the volume of the unit cell, \( C \) is the critical doped concentration of Mn⁴⁺, and \( N \) is the number of dopant sites available per unit cell. In the BLMN:0.4% Mn⁴⁺ case, the \( C = 0.4\% \); \( V = 523.99 \text{ Å}^3 \); \( N = 4 \). Thus, \( R_c \) was calculated to be about 39.69 Å. Because the exchange interaction is possible only when the \( R_c \) is smaller than 5 Å, so the electric multipolar interaction was the major mechanism of the energy transfer between Mn⁴⁺ ions in BLMN host. Furthermore, the detailed concentration quenching mechanism can be analyzed by the following equation:⁵⁵

\[ \log(I/x) = A - (\theta/3)\log x \]  

(3)

where \( I \) is the emission intensity, \( x \) is the activator ion concentration, \( A \) is concentration and the values of \( \theta = 6, 8 \) and
10 correspond to electric dipole–dipole, dipole–quadrupole and quadrupole–quadrupole interaction, respectively. Fig. 5(d) shows the dependence of \( \log(I/x) \) on \( \log(x) \) of the BLMN: \( x \text{Mn}^{4+} \) phosphors. The slope of the fitting line was \(-1.4270\). Thus \( \theta = 4.281\), which was close to 3, which inferred that the concentration quenching mechanism of BLMN: \( x \text{Mn}^{4+} \) was the non-radiative energy transfer among the adjacent \( x \text{Mn}^{4+} \) ions.

The Commission International de l’Eclairage (CIE) coordinates of the BLMN:0.4% \( x \text{Mn}^{4+} \) sample were calculated on the basis of its PL emission spectrum and the corresponding results are displayed in Fig. 6(a). The CIE chromaticity coordinates of the BLMN:0.4% \( x \text{Mn}^{4+} \) sample were determined to be \((0.7222, 0.2777)\) under the excitation of 360 nm. The inset shows the digital images of the as-synthesized BLMN:0.4% \( x \text{Mn}^{4+} \) sample under daylight and 365 nm UV light. The BLMN:0.4% \( x \text{Mn}^{4+} \) sample showed a bright far-red light. These results revealed that the BLMN: \( x \text{Mn}^{4+} \) phosphors may be promising candidates as far-red-emitting materials for plant growth LEDs. Under 360 nm excitation, the IQE of BLMN:0.4% \( x \text{Mn}^{4+} \) sample was measured and illustrated in Fig. 6(b). The IQE value of the BLMN:0.4% \( x \text{Mn}^{4+} \) sample was calculated by using the following equation:68

\[
\eta = \frac{\int L_s}{\int E_R - \int E_S}
\]  

where \( \eta \) is IQE, \( L_s \) is the emission spectrum of the sample, \( E_S \) and \( E_R \) are the spectra of excitation light with sample and only with \( \text{BaSO}_4 \) reference, respectively. Hence, the IQE value of as-prepared BLMN:0.4% \( x \text{Mn}^{4+} \) sample reached as high as 52%, which was higher than many recently reported \( x \text{Mn}^{4+} \)-activated red-emitting phosphors, such as \( x \text{SrLaScO}_4: \text{Mn}^{4+} \) (IQE: 12.2%), \( x \text{Li}_2\text{Mg}_3\text{SnO}_6: \text{Mn}^{4+} \) (IQE: 36.3%), \( x \text{Li}_2\text{MgZrO}_4: \text{Mn}^{4+} \) (IQE: 32.3%), \( x \text{Ba}_2\text{YNbO}_6: \text{Mn}^{4+} \) (IQE: 29.2%).

Fig. 7 shows the decay curves of BLMN: \( x \text{Mn}^{4+} \) (\( x = 0.05\%\), 0.1\%, 0.2\%, 0.4\%, 0.8\%, and 1.0\%) phosphors monitored at 700 nm with an excitation wavelength of 360 nm. All of the decay curves were fitted with a single-exponential equation:61

\[
I_t = I_0 \exp(-t/\tau) + A
\]

where \( I_t \) and \( I_0 \) are the luminescence intensities at time \( t \) and \( t = 0 \), respectively; \( \tau \) represents the decay time for the exponential components; and \( A \) is a constant. Based on the above equation, the lifetimes of BLMN: \( x \text{Mn}^{4+} \) (\( x = 0.05\%\), 0.1\%, 0.2\%, 0.4\%, 0.8\%, and 1.0\%) phosphors were determined to be 0.783, 0.760, 0.753, 0.733, 0.677, and 0.652 ms, respectively. As can be seen, with increasing \( x \text{Mn}^{4+} \) doping concentrations form 0.05% to 1.0%, the lifetimes declined monotonously. This was because...
that the non-radiative energy migration among the Mn$^{4+}$–Mn$^{4+}$ pairs became more faster.$^{62–64}$

The luminescence mechanism has been analyzed by Tanabe–Sugano energy level diagram of Mn$^{4+}$ ion in the octahedral site, as shown in Fig. 8. Mn$^{4+}$ ion with a 3d$^3$ electronic configuration belongs to transition metal ion. When excited at 375, 472, and 520 nm, the electrons at ground state 4A$_{2g}$ were pumped to the excited states 4T$_{1g}$, 2T$_{2g}$, and 4T$_{2g}$, after that the excited electrons can relax to the lowest excited state 2E$_g$ by non-radiative transition process. Finally, the electrons from the lowest excited state 2E$_g$ back to ground state may occur, thus resulting in far-red light centered at 700 nm. Crystal field intensity (D$q$) can be roughly calculated using the peak energy (19 231 cm$^{-1}$) of the 4A$_{2g}$ $\rightarrow$ 4T$_{2g}$ transition by the following equation:$^{65–67}$

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

thus the value of $D_q$ was 1923 cm$^{-1}$. The Racah parameter $B$ can be estimated according to the equation:$^{68}$

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

where $x$ is defined as follow:$^{69}$

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

by using the peak energy (26 667 cm$^{-1}$) of 4A$_{2g}$ $\rightarrow$ 4T$_{1g}$ transition and 4A$_{2g}$ $\rightarrow$ 4T$_{2g}$ (19 231 cm$^{-1}$), the value of $B$ was then determined to be 736 cm$^{-1}$. Thus, $D_q/B$ value can be calculated to be 2.61, which was beyond 2.2, indicating Mn$^{4+}$ ions located in a strong crystal field. In additional, another Racah parameter $C$ can be evaluated using following equation:$^{70}$

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

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**Fig. 6** (a) CIE chromaticity coordinates of BLMN:0.4% Mn$^{4+}$ phosphors ($\lambda_{ex}$ = 360 nm). Inset shows the digital images of BLMN:0.4% Mn$^{4+}$ in daylight and under a 365 nm UV lamp. (b) Excitation line of BaSO$_4$ and the PL spectrum of BLMN:0.4% Mn$^{4+}$ phosphor collected using an integrating sphere.

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**Fig. 7** Decay curves of BLMN:xMn$^{4+}$ ($x$ = 0.05%, 0.1%, 0.2%, 0.4%, 0.8%, and 1.0%) phosphors monitored at 700 nm with an excitation wavelength of 360 nm.

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**Fig. 8** Tanabe–Sugano energy-level diagram of Mn$^{4+}$ in the octahedral site of BLMN host.
according to the peak energy (14 286 cm\(^{-1}\)) of \(^2E_g \rightarrow ^4A_{2g}\) transition, the value for \(C\) was evaluated to be 2944 cm\(^{-1}\).

According to the Tanabe–Sugano energy-level diagram, the wide variation in the energy of the \(^2E_g \rightarrow ^4A_{2g}\) transition was barely dependent on crystal field strength. It should be determined mainly by the nephelauxetic effect, which was related to the variation in the Racah parameters \(B\) and \(C\). Brik et al. introduced a new parameter that described the nephelauxetic effect \(\beta_1\).\(^{70,71}\)

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

(10)

where the free ion values \(B_0\) and \(C_0\) for the Mn\(^{4+}\) are 1160 cm\(^{-1}\) and 4303 cm\(^{-1}\), respectively. \(B\) and \(C\) are the Racah parameters of Mn\(^{4+}\) in BLMN host. In the BLMN host the \(\beta_1\) for Mn\(^{4+}\) was determined to be 0.93. Brik et al. fitted a liner relationship between the energy of the emission (\(^2E_g \rightarrow ^4A_{2g}\) transition) and \(\beta_1\), the equation is \(E^\prime(\beta_1) = -880.49 + 16261.92\beta_1 + \sigma\), where the \(\sigma\) (332 cm\(^{-1}\)) represents the root-mean-square (rms) deviation of the data points from the fit line.\(^{72}\) The calculated \(^2E_g\) energy level was 13 911–14 575 cm\(^{-1}\). The experimental energy value for the \(^2E_g \rightarrow ^4A_{2g}\) transition of Mn\(^{4+}\) in the BLMN host was 14 286 cm\(^{-1}\). Obviously, the result was in accord with the linear line and thus it was reliable.

Fig. 9(a) shows the temperature-dependent emission spectra of BLMN:0.4% Mn\(^{4+}\) phosphors in the temperature range of 303–463 K under the excitation of 360 nm. It could be observed that with increasing the temperature, the peaks shape and position were almost similar. Moreover, the normalized intensity trend of the BLMN:0.4% Mn\(^{4+}\) was also shown in Fig. 9(b).

With increasing temperature, the PL emission intensity decreased gradually due to the temperature quenching effect. To better understand the thermal quenching characteristics, the activation energy \(E_a\) was evaluated using the following equation:\(^{21}\)

\[
\ln\left(\frac{I_o}{I} - 1\right) = \ln A - \frac{E_a}{kT},
\]

(11)

where \(I_o\) is the initial emission intensity, \(I\) is the intensity at different temperatures, \(k\) is the Boltzmann coefficient, \(A\) is the constant, \(E_a\) is activation energy. Linear relationship between \(\ln(I_o/I - 1)\) and \(1/kT\) is depicted in Fig. 9(c). The experimental data could be linear fitted with a slope of \(-0.411\), so the value of \(E_a\) was obtained to be 0.411 eV.

In order to further demonstrate the potential application value of the BLMN: Mn\(^{4+}\) phosphors in LEDs for indoor plant growth, a far-red LED device was fabricated by using as-obtained BLMN:0.4% Mn\(^{4+}\) phosphors coated onto a 365 nm near-UV InGaN chip. Fig. 10 shows the electroluminescent (EL) spectrum of the as-prepared LED device under the driven current of 60 mA. As shown in the inset of Fig. 10, it could be seen that the fabricated LED device clearly exhibited bright far-red light, which was attributed to a narrow emission band peaking at about 700 nm due to the \(^2E_g \rightarrow ^4A_{2g}\) transition of Mn\(^{4+}\) ions in BLMN host. The CIE chromaticity coordinates of the LED was (0.7109, 0.2890). In this work, the device has low luminous efficacy of 0.02 lm W\(^{-1}\). Compared with plants, the ability of human eye to perceive of far red light is weaker, resulting in low luminous efficacy. These results indicated that the BLMN:Mn\(^{4+}\) could be considered as far-red-emitting phosphors for plant growth LEDs.

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**Fig. 9** (a) Temperature-dependent PL spectra of BLMN:0.4% Mn\(^{4+}\) phosphors under the excitation at 360 nm. (b) The dependence of the normalized emission intensity as a function of temperature. (c) Linear relationship between \(\ln(I_o/I - 1)\) and \(1/kT\) and the calculated activation energy (\(E_a\)) for the phosphors.

**Fig. 10** EL spectrum of the fabricated far-red LED device by using BLMN:0.4% Mn\(^{4+}\) phosphors and a 365 nm near-UV InGaN chip under a current of 60 mA. Inset shows the fabricated LED device and corresponding luminescent image.
Conclusions

In summary, novel far-red-emitting BLMN:Mn$^{4+}$ phosphors were successfully synthesized by the conventional high-temperature solid-state reaction method. The Rietveld refinement results indicated that the structure of sample was a cubic system in space group $Fm\overline{3}m$. Monitored at 700 nm, two broad absorption bands were shown between 250 and 600 nm. With excitation of 360 and 469 nm, a far-red emission located at 700 nm within the range of 650–800 nm attributed to the $^2E_g \rightarrow ^4A_{2g}$ transition of Mn$^{4+}$ ions, which was matched well with the absorption spectra of phytochrome $P_{FR}$. The optimal Mn$^{4+}$ doping concentration was about 0.4 mol%, and the concentration quenching mechanism of BLMN:Mn$^{4+}$ was the non-radiative energy transfer among the adjacent Mn$^{4+}$ ions. The CIE chromaticity coordinates and IQE of BLMN:0.4% Mn$^{4+}$ sample were (0.7222, 0.2777) and 52%, respectively. In addition, the crystal field strength $D_q$, the Racah parameters $B$ and $C$ were calculated. The value of activation energy $E_a$ was 0.411 eV. Finally, a far-red LED was fabricated by using BLMN:0.4% Mn$^{4+}$ phosphors and a 365 nm near-UV LED chip. The obtained results demonstrate the BLMN:Mn$^{4+}$ phosphors could be red-emitting phosphors for far-red LEDs for plant cultivation field.

Conflicts of interest

There are no conflicts to declare.

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