Red Phosphor Rb$_2$NbOF$_5$:Mn$^{4+}$ for Warm White Light-Emitting Diodes with a High Color-Rendering Index

Zhengliang Wang,‡,‡ Zhiyu Yang,‡ Zhaofeng Yang,‡ Qianwen Wei,‡ Qiang Zhou,‡ Li Ma,‡ and Xiaojun Wang*‡‡

ABSTRACT: We successfully prepared a red-emitting phosphor Rb$_2$NbOF$_5$ doped with Mn$^{4+}$, and investigated its crystal structure, luminescent properties, and applications in detail. Mn$^{4+}$ ions in Rb$_2$NbOF$_5$ exhibit an intense red emission with high color purity upon a broad excitation in the blue region. The related crystal-field parameters of Mn$^{4+}$ in Rb$_2$NbOF$_5$ have been estimated according to the luminescent spectra. More importantly, Rb$_2$NbOF$_5$:Mn$^{4+}$ has high thermal-quenching resistance and color stability. We further fabricated a warm white light-emitting diode using the phosphor, emitting intense white light with a high color-rendering index of 90 and a low color temperature of 3418 K. The results indicate that Rb$_2$NbOF$_5$:Mn$^{4+}$ is a potential red-emitting phosphor for white light-emitting diodes.

INTRODUCTION

Over the years, red-emitting phosphors have attracted more and more attention as a critical component for white light-emitting diodes (w-LEDs).1–3 There is a need to optimize the optoelectronic performances of w-LEDs with a low color temperature ($T_c$) and a high color-rendering index ($R_e$) for indoor lighting. Recently, non-rare-earth Mn$^{4+}$-activated phosphors have been studied as important candidates for the purpose because of their unique photoluminescent (PL) properties in an octahedral crystal field.4–7 Mn$^{4+}$ in oxide hosts can emit a deep red light with moderate intensity in the range of 650–720 nm under UV or blue light excitation.8–11 On the other hand, Mn$^{4+}$-activated fluoride phosphors (such as hexafluoride phosphors A$_2$BF$_6$:Mn$^{4+}$; A = Na, K, Rb, Cs; B = Si, Ti, Ge) exhibit intense emission around 630 nm with high color purity for w-LEDs.12–22 In view of developing new Mn$^{4+}$-activated phosphors, oxyfluorides are good hosts for doping Mn$^{4+}$ ions.

Recently, a few such red-emitting phosphors have been reported, such as Cs$_5$WO$_2$F$_3$:Mn$^{4+}$ by Cai et al.23 and Na$_x$WO$_2$F$_2$:Mn$^{4+}$ by Wang’s groups.24 Mn$^{4+}$ ions in both oxyfluorides can yield an intense red emission with a broad excitation band in the blue light region. Moreover, the PL properties of Cs$_x$NbOF$_5$ and BaNbOF$_5$ doped with Mn$^{4+}$ were also reported recently.25–27 Hence, it is interesting and significant to develop new Mn$^{4+}$-activated red phosphors based on oxyfluorides.

The oxo-fluoroniobate complex Rb$_2$NbOF$_5$ (denoted as RNOF) is a type of d$^0$ transition metal oxyfluoride compound (A$_2$MO$_x$F$_{6-x}$; A = Na, K, Rb, Cs; x = 1 for M = V, Nb, Ta; x = 2 for M = W and Mo).28 To the best of our knowledge, the PL properties of RNOF:Mn$^{4+}$ have never been investigated. Herein, we report the preparation, characterization, and PL studies of the red-emitting phosphor Rb$_2$NbOF$_5$:Mn$^{4+}$. We have further fabricated a prototype white-emitting diode with improved color indexes.

EXPERIMENTAL SECTION

Materials and Synthesis. All raw materials and reagents including hydrogen fluoride (HF), Nb$_2$O$_5$, RbF, HC$_2$O$_4$, and CH$_3$OH were of analytical grade and used without further purification. The commercial yellow Y$_3$Al$_5$O$_{12}$:Ce$^{3+}$ (YAG:Ce$^{3+}$) phosphor was purchased from Quanjing Photon Co. Ltd, (Shenzhen, China). K$_2$MnF$_6$ was from our previous work.29 Phosphors RNOF:xMn$^{4+}$ ($x = 0.001, 0.005, 0.01, 0.015,$ and 0.02) were synthesized by two-step reactions in HF liquid phase. The host RNOF was synthesized in the first step. For a typical reaction of RNOF (9.37 g), 25 mmol (3.32 g) of Nb$_2$O$_5$ were dissolved into 50 mL of HF (40 wt %) at 80 °C. Then, 0.15 mol (15.7 g) of RbF were added into the above solution with stirring for 2 h. The RNOF host was obtained by evaporating the extra HF in a fume cupboard. The second step was to dope Mn$^{4+}$ in RNOF by an ion-exchange method. Using RNOF:0.01 Mn$^{4+}$ preparation as an example, 2.5 mmol (0.937 g) of freshly prepared RNOF and 0.025 mmol (0.006 g) of K$_2$MnF$_6$ were added into the above solution with stirring for 2 h. The Mn$^{4+}$ ions in RNOF were replaced by Mn$^{4+}$ ions in K$_2$MnF$_6$. The resulting solution was allowed to stand for 2 days and then filtered.

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were added into a 5 mL solution of H2O and CH3OH (50:1 volume ratio) with magnetic stirring for 3 h. The precipitates were washed three times with ethanol and dried at 60 °C for 12 h. A series of RNOF:xMn4+ samples with different Mn4+ concentrations were prepared by changing the amount of K2MnF6 used in the second reaction step.

Fabrication of LED Devices. According to our previous work,79 a number of LED devices were fabricated by coating as-selected red phosphor Rb2NbOF4:Mn4+ on blue GaN-LED chips with or without yellow phosphor YAG:Ce3+.

Characterizations. The X-ray diffraction (XRD) pattern of the sample was measured by powder X-ray diffraction (D8 Advance, Bruker, Germany). SEM images were obtained on a scanning electron microscope (SEM, FEI Quanta 200 Thermal FE Environment scanning electron microscopy) with an attached energy-dispersive X-ray spectrometer (EDX). The PL efficiencies were obtained on an FLS920 fluorescence spectrophotometer with low-temperature attachment. The quantum efficiencies were obtained on an F-7000 Fluorescence Spectrophotometer. The optical performance of these LED devices was collected on a highly accurate array spectrometer (HYPERSPECT, Horiba scientific) under 460 nm excitation by Surelile Laser pumped Horizon I and II OPO (Continuum). The PL spectrum was obtained on a Cary 5000 UV−vis−NIR spectrophotometer, and the decay curves were collected by a FluoroLog 3 TCSPC system (HORIBA scientific) under 460 nm excitation by Surelile Laser pumped Horizon I and II OPO (Continuum). The PL spectra were measured by a Cary Eclipse FL1011M003 (Varian) spectrofluorometer, and the emission spectrum was measured on an FLS920 fluorescence spectrophotometer with low-temperature attachment. The quantum efficiencies were obtained on an F-7000 Fluorescence Spectrophotometer. The optical performance of these LED devices was collected on a highly accurate array spectrometer (HYPERSPECT, Horiba scientific) under the following conditions: center field, 2500 G; scan range, 0−5000 G; field modulation, 5 G; microscope power, 0.6 mW; time constant, 10 ms.

■ RESULTS AND DISCUSSION

Structure, Morphology, and Composition Analysis. The XRD pattern of as-prepared RNOF:0.01 Mn4+ is shown in Figure 1a. All diffraction peaks of RNOF:0.01 Mn4+ can be well indexed corresponding to the JCPDS card (No. 43-0398) of RNOF with the hexagonal structure (a = b = 6.056 Å; c = 4.851 Å; V = 154.08 Å3). It is clear that RNOF:0.01 Mn4+ is of the same single phase with a hexagonal structure as RNOF and Mn3+ ions do not alter the host structure at 0.01 doping. In the crystal structure of RNOF, each Nb5+ is coordinated by five F− and one O2− to form a distorted octahedron of [NbOF5]2−.28 The inset in Figure 1a shows that Nb5+ ion moves from the center of [NbOF5]2− toward the oxide, resulting in a shorter Nb−O bond than that of Nb−F. This is because O2− is a good π-donating ligand that can form a strong bond with Nb5+.30 Considering the same charge and similar volumes of [NbOF5]2− and [MnF6]2−, the site of [NbOF5]2− in RNOF:0.01 Mn4+ will be occupied by [MnF6]2−, which will induce the structural defects with oxygen vacancies.26

The SEM image and EDX spectrum of RNOF:0.01 Mn4+ are both presented in Figure 1b. The SEM image indicates that RNOF:0.01 Mn4+ is composed of ∼2 μm particles with a clear surface and uniform size. All elements (Rb, Nb, O, F, and Mn) in RNOF:0.01 Mn4+ can be easily identified in the EDX spectrum. This is the evidence that manganese ions have been doped into the crystal lattices of RNOF:0.01 Mn4+.

PL Properties. RNOF:xMn4+ (x = 0.001, 0.005, 0.01, 0.015, and 0.02) are of similar PL spectra, as shown in Figure S1 in Supporting Information. Among these samples, RNOF:0.01 Mn4+ exhibits the strongest red emission around 631 nm upon excitation at 465 nm. Hence, we used concentration-optimized RNOF:0.01 Mn4+ for further studies in detail. The excitation spectrum (black line) and diffuse reflection spectrum (red line) of RNOF:0.01 Mn4+ are shown in Figure 2a. Two broad absorption bands around 360 and 465 nm, respectively, can be observed consistently from both excitation and diffuse reflection spectra. They are ascribed to the spin-allowed transitions of Mn4+ from the ground state 4A2 to excited states 4T1 and 4T2, respectively. The intense excitation band at ∼465 nm with a full width at half maximum of ∼50 nm can completely cover the emission of the blue LED chip (∼460 nm). The strongest excitation band (∼465 nm) shows a slight blue shift, compared with that of Cs2NbOF4:Mn4+ (∼474 nm).25,26 This result indicates that RNOF:0.01 Mn4+ possesses a stronger crystal field strength than Cs2NbOF4:Mn4+.

Figure 2b is the emission spectra of RNOF:0.01 Mn4+ under 465 nm light excitation at 298 and 13 K, along with its photograph irradiated by the blue light at room temperature (inset). In the emission spectrum at 298 K, the series of red-emitting peaks from 600 to 650 nm are due to the anti-Stokes ν3, ν4, and ν5 and Stokes ν3, ν4, and ν5 phonon side bands of E to 4A2, where the Stokes band is spin-forbidden transitions with the strongest peak at 631 nm. The zero phonon line (ZPL) of Mn4+ in RNOF:0.01 Mn4+ is hardly observed at room temperature because of the strong electron−phonon coupling. When the temperature is brought down to 13 K, a weak ZPL can be observed at 622 nm, as shown in Figure 2b.

Meanwhile, the intensity of anti-Stokes transitions decreases
The calculated values of \( B \) and \( C \) are \( 584 \) and \( 3852 \) cm\(^{-1}\) respectively, and the value of \( D_\parallel /B \) is \( 3.68 \). Hence, \( \text{Mn}^{4+} \) in \( \text{RNOF:0.01 Mn}^{4+} \) experiences a strong crystal field.

Recently, Brik’s group has proposed a new parameter \( \beta_1 \) to determine the energy of \( ^2E \rightarrow ^4A_2 \) transition of \( \text{Mn}^{4+} \).\(^{34}\) This parameter \( \beta_1 \) can be calculated as follows

\[
\beta_1 = \sqrt{\left( \frac{B}{B_0} \right)^2 + \left( \frac{C}{C_0} \right)^2} \tag{4}
\]

where \( B_0 \) (1160 cm\(^{-1}\)) and \( C_0 \) (4303 cm\(^{-1}\)) are the Racah parameters of free \( \text{Mn}^{4+} \).\(^{35}\) \( \beta_1 \) in \( \text{RNOF:0.01 Mn}^{4+} \) is calculated to be \( 1.027 \). Then, the energy level of \( ^2E \) can be estimated by the following equation\(^{34}\)

\[
E(\ ^2E) = -142.83 + 15544.02 \beta_1 + \sigma \tag{5}
\]

where the value of \( \sigma \) is 365 cm\(^{-1}\). The calculated energy value of \( ^2E \) (16 186 cm\(^{-1}\)) is close to the experimental measurement (16 077 cm\(^{-1}\)).

Figure 3 presents the EPR spectra of \( \text{RNOF:0.01 Mn}^{4+} \) obtained at room temperature (a) and 12 K (b). The \( \text{Mn}^{4+} \) ion has a 3d\(^3\) electronic configuration and the high spin state is \( S = 3/2 \). We interpret that, for curve (a), the axial spectrum with \( g_\perp = 1.994 \) and \( g_\parallel = 3.105 \) is the transition from the one of \( m_i = -1/2 \) to \( m_i = 1/2 \) state in an axial disordered octahedral crystal field. The weak feature at a low magnetic field around \( g = 6.532 \) is from the one of \( m_i = \pm 3/2 \) to \( \pm 1/2 \). This band assignment agrees well with the rhombogram of \( \text{Mn}^{4+} \) (\( S = 3/2 \)) system with a rhombicity of \( E/D = 0.36 \). Curve (b) is the spectrum collected at 12 K. The EPR band at low field is not pronounced at the low temperature of 12 K, further indicating that \( S = 1/2 \) is the ground state. As we know that the nuclear spin of Mn ions is \( 5/2 \), theoretically, six sets of nuclear hyperfine (NHF) exist and can be observed in most crystals with \( \text{Mn}^{2+} \) and \( \text{Mn}^{4+} \) centers. In fact, because of the low symmetry of the \( \text{Mn}^{4+} \) site and the anisotropic nature of the powder sample, the characteristic feature of \( \text{Mn}^{4+} \) NHF splitting is not clearly observed in \( \text{RNOF:0.01 Mn}^{4+} \). This phenomenon was observed in \( \text{Li}_{1-x}\text{Mn}_2\text{O}_4 \) and \( \text{Al}_2\text{O}_3 \)-supported manganese oxides reported by Stoyanova\(^{37} \) and Kijlstra,\(^{38} \) respectively. The separation of the first and last

and the anti-Stokes \( \nu_s \) peak disappears, as expected. According to this emission spectrum, the Commission Internationale de l’Eclairage (CIE) chromaticity coordinates are calculated to be \( x = 0.69 \) and \( y = 0.31 \). Apparently, the \( \text{RNOF:0.01 Mn}^{4+} \) can emit bright red light under blue light (460 nm) excitation with high color purity.

The luminescent behavior of \( \text{Mn}^{4+} \) in an octahedral crystal field can be interpreted by the Tanabe–Sugano energy-level diagram, as shown in Figure S2. The energies, \( E(4T_1) \) and \( E(4T_2) \), as increase as the crystal field strength around \( \text{Mn}^{4+} \) increases, but the energy of \( E(^2E) \) remains stable in the region with a stronger crystal field. According to the excitation and emission spectra of \( \text{RNOF:0.01 Mn}^{4+} \) (Figure 2), the \( ^4A_2 \rightarrow ^4T_2, ^4A_2 \rightarrow ^4T_1 \) and \( ^2E \rightarrow ^4A_2 \) transitions are about 21 505, 27 778, and 16 077 cm\(^{-1}\), respectively. Hence, we can estimate the crystal field strength \( (D_{q}) \) of \( \text{Mn}^{4+} \) in \( \text{RNOF:0.01 Mn}^{4+} \), which is about 2151 cm\(^{-1}\).\(^{31}\) The Racah parameters \( B \) and \( C \) can then be calculated using the following equations \(^{32,33,32,33} \)

\[
D_\parallel /B = 15(X - 8)/(X^2 - 10X) \tag{1}
\]

\[
E(\ ^2E)/B = 3.05C/B + 7.9 - 1.8B/D_\parallel \tag{2}
\]

where

\[
X = [E(4T_1) - E(4T_2)]/D_\parallel \tag{3}
\]
The hyperfine peaks have 370 G around a center g value of 1.994 as shown in curve (a), yielding an NHF splitting of about 62 G, which confirms the existence of Mn$^{4+}$ centers in RNOF phosphor.

In addition, the decay curves of transitions of $^2E \rightarrow {}^4A_2$ of Mn$^{4+}$ in RNOF:$x$Mn$^{4+}$ ($x = 0.001, 0.005, 0.01, and 0.015$) have been measured, as shown in Figure 4. These decay curves are well fitted into a single exponential decay equation, and the decay times were 5.02, 4.83, 4.73, and 4.61 ms, respectively. When the Mn$^{4+}$-doping concentration increases, the decay times decrease, indicating the increase of the nonradiative transition process between the Mn$^{4+}$−Mn$^{4+}$ pair. This result is in accordance with that of K$_2$TiF$_6$ doped with different concentrations of Mn$^{4+}$.

Besides, the quantum efficiencies of these samples are listed in Table S1. The internal quantum efficiency and external quantum efficiency of RNOF:0.01 Mn$^{4+}$ are 67.7 and 18.6%, respectively.

The thermal-quenching resistance of luminescence is an important parameter for phosphors that can be applied to w-LEDs, because the working temperature could be as high as 150 °C, and this seriously influences the luminous efficiency (LE) of w-LEDs. We have investigated the temperature dependence of the Mn$^{4+}$ luminescence intensity in RNOF:0.01 Mn$^{4+}$, as shown in Figure 5a. All of the emission spectra of RNOF:0.01 Mn$^{4+}$ at different temperatures exhibit similar shapes with six groups of emission peaks at the same positions. As the temperature increases, the integral emission intensity ($I_T$) of RNOF:0.01 Mn$^{4+}$ shows a rising trend and reaches a maximum at 80 °C accompanied by the strengthened intensities of anti-Stokes ($I_a$) from 550 to 622 nm and Stokes transitions ($I_s$) from 622 to 700 nm (Figure 5b). The initial intensity increase could be due to the electrons detrapped from the phosphor.

However, thermal quenching of the Mn$^{4+}$ emission happens when the temperature exceeds 80 °C. In addition, the thermal-quenching energy ($E_q$) of RNOF:0.01 Mn$^{4+}$ can be calculated using the modified Arrhenius equation (eq 6) according to the temperature dependence of the emission intensity between 80 and 160 °C:

$$I_T = \frac{I_0}{1 + A \exp \left( \frac{-E_q}{kT} \right)}$$

where $I_0$ and $I_T$ are the emission intensities of RNOF:0.01 Mn$^{4+}$ at 80 °C and at any given temperatures $T$, respectively. $A$ is a constant and $k$ is the Boltzmann constant ($8.629 \times 10^{-5}$ eV K$^{-1}$). $E_q$ is then calculated to be 1.11 eV (8952 cm$^{-1}$), which is close to 1.20 eV (9677 cm$^{-1}$) for Cs$_2$NbOF$_5$:Mn$^{4+}$, 1.13 eV (9143 cm$^{-1}$) for K$_2$TiF$_6$:Mn$^{4+}$, and larger than that of BaNbOF$_5$:Mn$^{4+}$ (0.506 eV, 4941 cm$^{-1}$).
Figure 5c depicts the CIE chromaticity coordinates based on the emission spectra of RNOF:0.01 Mn⁴⁺ at different temperatures. As the temperature increases, the CIE coordinates (x, y) show a slight shift. Between 20 and 160 °C, the variation values of the CIE coordinates (Δx and Δy) are 0.014 and 0.014, indicating that RNOF:0.01 Mn⁴⁺ has excellent color stability in this temperature range. Hence, RNOF:0.01 Mn⁴⁺ could find potential applications in w-LEDs, especially when the thermal-quenching performance gets improved at higher temperatures (T > 100 °C).

**Application in LED Devices.** To demonstrate the improved performance of w-LEDs by coating RNOF:0.01 Mn⁴⁺, we fabricated and investigated the luminescent properties of w-LEDs coated with commercial YAG:Ce³⁺ only and with mixtures of YAG:Ce³⁺ and RNOF:0.01 Mn⁴⁺ on blue GaN chips. Figure 6 presents the luminescent spectra of a series of LED devices under 20 mA working current. Spectrum (a) is collected from a single GaN LED chip, giving a broad blue emission around 460 nm. After coating RNOF:0.01 Mn⁴⁺, six groups of red-emitting peaks and the less intense blue band of the chip can be observed in spectrum (b) (pink LED). Curves (c) and (d) in Figure 6 are the spectra of YAG:Ce³⁺-coated w-LEDs without and with red-phosphor RNOF:0.01 Mn⁴⁺, respectively. The bluish white light in (d) becomes warmer with the additional coating of RNOF:0.01 Mn⁴⁺, indicating that Rb₂NbOF₅:Mn⁴⁺ has potential applications for w-LEDs.

![Figure 6](image)

**CONCLUSIONS**

A red-emitting phosphor Rb₂NbOF₅:Mn⁴⁺ was prepared using the ion-exchange method. The as-obtained samples have a single phase with the hexagonal structure. This phosphor can emit intense red light with high color purity and a broad excitation band that perfectly overlaps the blue emission of the GaN chip. The as-prepared phosphor presents high thermal-quenching resistance and excellent color stability. The warm w-LED fabricated with Rb₂NbOF₅:Mn⁴⁺ exhibits excellent optical performances (Rg = 90), indicating that Rb₂NbOF₅:Mn⁴⁺ phosphor has potential applications for w-LEDs.

**ASSOCIATED CONTENT**

Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acs.inorgchem.8b02676.

- PL spectra, and Tanabe–Sugano energy-level diagram and PL quantum efficiencies (PDF)

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Notes

The authors declare no competing financial interest.

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**REFERENCES**


**Table 1. Important Photoelectric Parameters for LED Devices under 20 mA Current**

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<th>Phosphor</th>
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**Table 1. Important Photoelectric Parameters for LED Devices under 20 mA Current**

**Figure 6.** (a) Luminescent spectra of LED chip, (b) pink-emitting LED based on RNOF:0.01 Mn⁴⁺, (c) w-LED based on YAG:Ce³⁺, and (d) w-LED based on the mixture of YAG:Ce³⁺ and RNOF:0.01 Mn⁴⁺ under 20 mA current.