



Novel Mn⁴⁺-activated oxyfluoride Cs₂NbOF₅:Mn⁴⁺ red phosphor for warm white light-emitting diodes

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ABSTRACT

Novel red-emitting phosphor Cs₂NbOF₅:Mn⁴⁺ was prepared via the ion exchange method, and its crystal structure, composition and morphology were characterized by powder X-ray diffraction, energy-dispersive X-ray spectroscopy and scanning electron microscopy. Meanwhile, the influence of Mn⁴⁺ molar ratio on luminescence properties of Cs₂NbOF₅:Mn⁴⁺ has been investigated. The phosphor prepared with the Nb₂O₅/K₂MnF₆ molar ratio of 20:1 can emit intense red light under blue light excitation and improve the performances of white light-emitting diode with high color rendering index of 88.4 and low correlated color temperature of 3631 K, so this new red-emitting phosphor could find application on solid-state emitting diode.

1. Introduction

Phosphor-converted white-light-emitting diodes (WLEDs) can be widely used in solid-state illumination and the backlight of liquid crystal display, because of their unique advantages (high efficiency, low power consumption, etc.) [1–3]. Red-emitting phosphor is an important component for WLEDs, which can optimize the performances of WLEDs. Recently, Mn⁴⁺-activated phosphors as important candidates for red-emitting phosphors have been studied in detail, due to their excellent photo-luminescent (PL) properties [4–8]. For example, Mn⁴⁺-activated fluoride phosphors, A₂XF₆:Mn⁴⁺ (A = K, Cs, Rb; X = Ti, Si and Ge), exhibit a series of red-emitting peaks with high color purity and broad excitation band which can perfectly cover the blue emission of GaN chip [6–12]. Meanwhile, Mn⁴⁺ ions in oxides also share intense red-emission under UV light or blue light excitation [13–15]. So, it is expected that Mn⁴⁺ will share similar PL properties in some oxyfluorides.

Recently, Cai et al. successfully synthesized the red phosphor Cs₂WO₂F₄:Mn⁴⁺ and investigated its PL properties [16]. This red-emitting phosphor shows intense emission at 632 nm Na₂WO₂F₄:Mn⁴⁺ was also prepared by Wang's group [17]. Mn⁴⁺ ion in such oxyfluorides has an ultra-intense zero phonon line. The excellent PL properties of Na₂WO₂F₄:Mn⁴⁺ mean that this phosphor has great potential in WLED lighting and display applications. Hence, it is interesting to develop new Mn⁴⁺-activated red-emitting phosphors using oxyfluoride.

In current work, we chose Cs₂NbOF₅ as the host for doping Mn⁴⁺ ions [18,19] and successfully prepared new red-emitting phosphor Cs₂NbOF₅:Mn⁴⁺ (CNOFM) through the ion exchange. The as-prepared CNOFM exhibits intensive red emission under blue light excitation. Warm WLEDs can be obtained by coating this red-emitting phosphor and commercial yellow phosphor Y₃Al₅O₁₂:Ce³⁺ (YAG:Ce³⁺) on blue GaN chips.

2. Experimental

All raw materials in this work are of analytical grade. The commercial YAG:Ce³⁺ yellow phosphor was purchased from Shenzhen Quanjing Photon Co. Ltd, China. K₂MnF₆ was prepared according to reference [20]. The synthesis procedure of CNOFM is shown in Fig. 1. Using CNOFM with the Nb₂O₅/K₂MnF₆ molar ratio of 20:1 as an example, we dissolved 2.5 mmol Nb₂O₅ into 2.5 mL HF (40 wt%) with magnetic stirring until the solution becomes transparency. Then, 0.125 mmol K₂MnF₆ was put into this transparent solution. 30 mmol CsF was added into the above solution in the next step. After stirring for 60 min at 50 °C, the precipitates were collected, washed with absolute alcohol for several times and dried at 80 °C. CNOFM samples with different molar ratios of Nb₂O₅ to K₂MnF₆ (60:1, 40:1, 15:1 and 10:1) were also prepared according to the same process. A set of LED devices were fabricated by coating the as-prepared red phosphor together with

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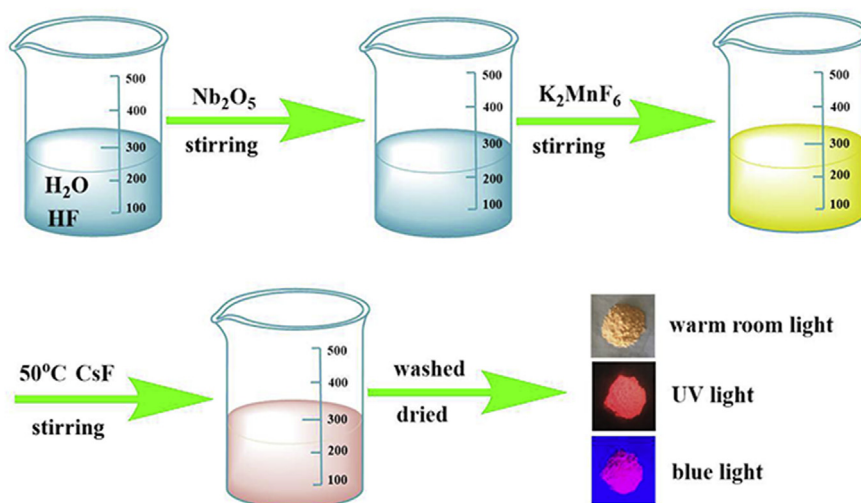


Fig. 1. Synthesis procedure of CNOFM phosphor.

YAG:Ce³⁺ on blue GaN LED chips.

X-ray diffraction (XRD) patterns of CNOFM were measured on a powder X-ray diffraction (D8 Advance, Bruker, Germany). Scanning electron microscopy (SEM) image was taken on a scanning electron microscopy (SEM, FEI Quanta 200 Thermal FE Environment Scanning Electron Microscopy) with an attached energy-dispersive X-ray (EDX) spectrometer. The doping amount of Mn⁴⁺ in Cs₂NbOF₅:Mn⁴⁺ was measured on a Shimadzu AA-6300 atomic absorption spectrophotometer (AAS). The diffuse reflectance spectrum (DRS) was obtained on a Cary 5000UV-Vis-NIR spectrophotometer. The PL spectra were measured by a Cary Eclipse FL1011M003 (Varian) spectrofluorometer. The performance of the LED devices was collected on a high accurate array spectrometer (HSP6000).

3. Results and discussion

Fig. 2a is the XRD patterns of CNOFM prepared with different molar ratios of Nb₂O₅ to K₂MnF₆ (60:1, 40:1, 20:1, 15:1 and 10:1). All the patterns are of similar shapes and consistent with the JCPDS card (No. 45–0940) of Cs₂NbOF₅ (hexagonal structure: $a = b = 6.31 \text{ \AA}$, $c = 5.02 \text{ \AA}$) [19]. No any other phases can be observed in these patterns, indicating that each sample is of pure single-phase and the doping of Mn⁴⁺ does not obviously change the structure of Cs₂NbOF₅ host. In the structure of Cs₂NbOF₅, each Nb⁵⁺ is coordinated by five F⁻ and one O²⁻ to form a disordered octahedron of [NbOF₅]²⁻. Thus, it is expected that Mn⁴⁺ occupies the site of Nb⁵⁺ in CNOFM. Fig. 2b is the EDX spectrum of CNOFM with the Nb₂O₅/K₂MnF₆ molar ratio of 20:1. The elements of O, F, Nb, Cs, and Mn can be easily found from this spectrum, but the element K cannot be observed, indicating that this sample does not contain any potassium impurity. The SEM image in the inserted picture in Fig. 2b shows that the particle size of this sample is about 30 μm. Very clear edges, corners and smooth surface of the particles can be observed, implying that those can be characterized by crystal habits.

Fig. 3 is the PL excitation (PLE) and diffuse reflectance spectra of CNOFM with the Nb₂O₅/K₂MnF₆ molar ratio of 20:1. Curve a is the PLE spectrum of the as-prepared sample by monitoring at 632 nm emission. This red phosphor has two intense broad excitation bands in the UV and blue regions 300–550 nm, which are due to the transitions of ⁴A_{2g} - ⁴T_{1g} and ⁴A_{2g} - ⁴T_{2g} of Mn⁴⁺, respectively. The strongest excitation band at ~470 nm completely covers the emission of the blue GaN chip (~460 nm), indicating that the as-prepared phosphor can be efficiently excited by blue LED chip. The DRS of CNOFM is also composed of two broad absorption bands, which are in good agreement with the PLE spectrum.

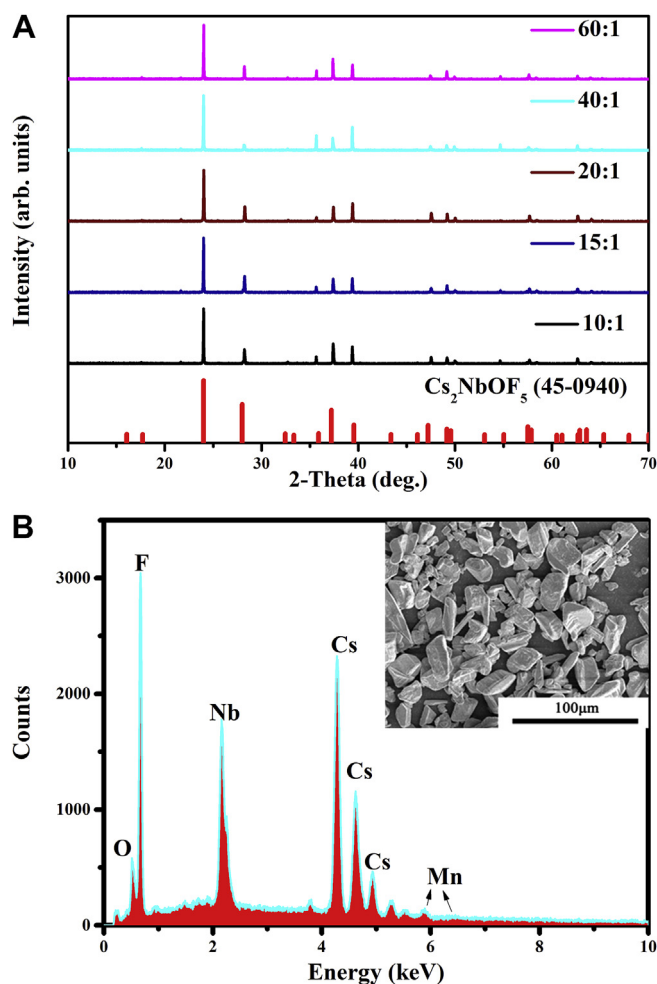


Fig. 2. XRD patterns of CNOFM prepared with different molar ratios of Nb₂O₅ to K₂MnF₆ (a), EDX spectrum of CNOFM with the Nb₂O₅/K₂MnF₆ molar ratio of 20:1 (b).

Fig. 4 shows the emission spectra of CNOFM samples prepared with different molar ratios of Nb₂O₅ to K₂MnF₆ under 470 nm light excitation. These phosphors are of similar emission spectra originating from the ²E_g → ⁴A_{2g} spin-forbidden transitions of Mn⁴⁺. These red-emitting peaks located at ~601, 610, 615, 632, 636 and 648 nm are ascribed as

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